CHEMISTRY LETTERS, pp. 947-950, 1989.

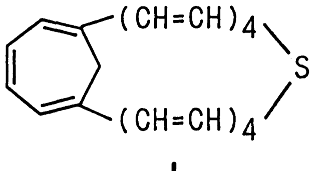
10,15-Methanothia[23]annulene. Geometrical Isomerism and Flipping of the Methylene Bridge

Gaku YAMAMOTO,* Jūro OJIMA,*† Hiroki MIYASHITA,†
Shigeyasu KURODA,†† and Yoshinari KANO††
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo 113
†Department of Chemistry, Faculty of Science,
Toyama University, Gofuku, Toyama 930
††Department of Industrial Chemistry, Faculty of Engineering,
Toyama University, Gofuku, Toyama 930

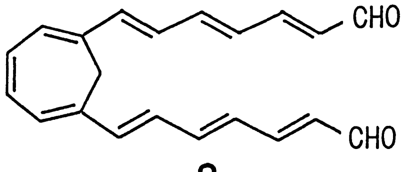
Synthesis of the title compound is described. The compound is composed of two geometrical isomers in which the positions of <u>cis</u> double bonds are different. Flipping of the methylene bridge is detected by dynamic NMR spectroscopy in both isomers.

Conformational mobility of annulenes is an interesting topic.1) We have studied methano-bridged annulenes which contain one or two cycloheptatriene moieties.2) In these compounds, flipping of the methylene bridge above and below the average plane of the macrocycle, or, in other words, ring inversion of the cycloheptatriene moiety, may be possible, but detailed dynamic NMR studies have not been made. The height of the flipping barrier depends on the ring-size and the rigidity of the macrocycle, and the detailed analysis of the barrier will give some information on the rigidity and the tropicity of the annulenes.

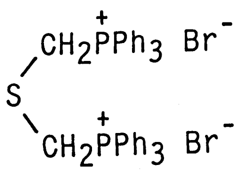
We now report the synthesis and ^1H NMR spectroscopic studies of 10,15-methanothia[23]annulene (**1**), which reveals geometrical isomerism and energy barriers to flipping of the methylene bridge. It should be mentioned that the compound is the largest heteroannulene hitherto synthesized that clearly shows a ring current effect.3)



1



2



3

A double Wittig reaction between 1,6-bis(6-formylhexa-1,3,5-trienyl)cyclohepta-1,3,5-triene (**2**)2e) and a slight excess of bis[(triphenylphosphonio)methyl] sulfide dibromide (**3**)4) with ethanolic lithium ethoxide at 70 °C in DMF afforded 10,15-methanothia[23]annulene (**1**) as relatively unstable black purple needles in 6.5% yield: mp 164 °C (dec); Found: C, 83.25; H, 6.65%. Calcd for $C_{23}H_{22}S$: C,

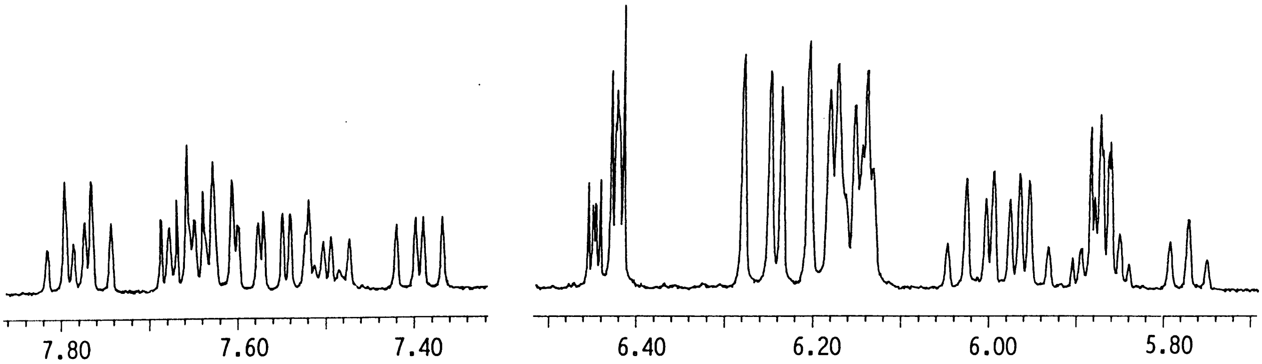


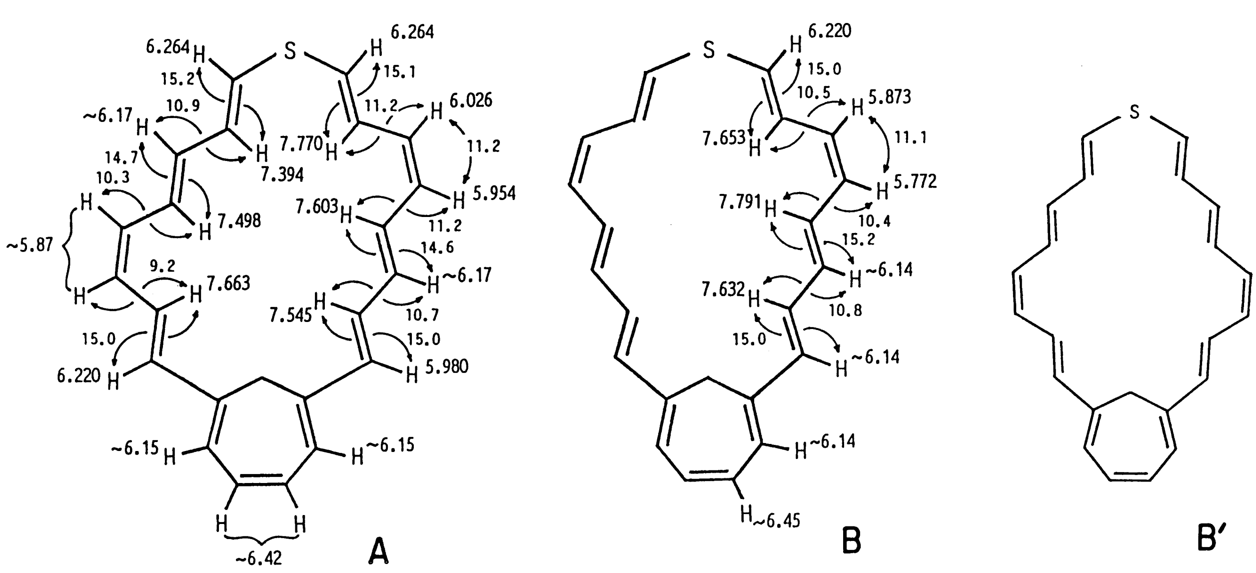
Fig. 1. The olefinic proton region of the 500 MHz ^{1}H NMR spectrum of a mixture of two isomers of 1 (**A**/**B** = 1.7) in $CDCl_3$ at 20 °C.

83.59; H, 6.71%; MS m/z 330 (M^+, 100%); IR (KBr) 960 (trans C=C), 740 and 730 cm^{-1} (cis C=C); UV (THF) 340 sh (ε 82700), 352 (98000), and 463 nm (sh, 1700).

^{1}H NMR shows that compound **1** thus obtained is a mixture of two isomers. The isomer ratio in $CDCl_3$ solution is 1.3-3.0 depending on the samples prepared under different conditions and slowly approaches an equilibrium ratio of <u>ca</u>. 2.0 when left standing several days at room temperature, accompanied by considerable thermal decomposition.[5,6]

Careful examination of the olefinic proton region of the 500 MHz ^{1}H NMR spectra of the isomer mixture (Fig. 1) including decoupling experiments allowed us structural and chemical shift assignments (Scheme 1). The major isomer shows six diastereotopic protons in a low-field region of δ 7.3-7.9 and ten diastereotopic protons in a high-field region of δ 5.7-6.5 indicating an unsymmetric structure, while the minor isomer has three kinds of protons in the low field region and five kinds of protons in the high field region, suggesting a symmetric structure.

The compound is a 24π-electron system and should be paratropic and thus the inner olefinic protons of the macrocycle are expected to appear at a lower field than the outer protons. The two isomers are therefore geometrical isomers in



Scheme 1.

which the positions of the cis double bonds are different. Structure **A** is unambiguously assigned to the major isomer from the coupling patterns[7] while structure B is tentatively assigned for the minor isomer although another symmetric structure B' can not be completely excluded.[7,8]

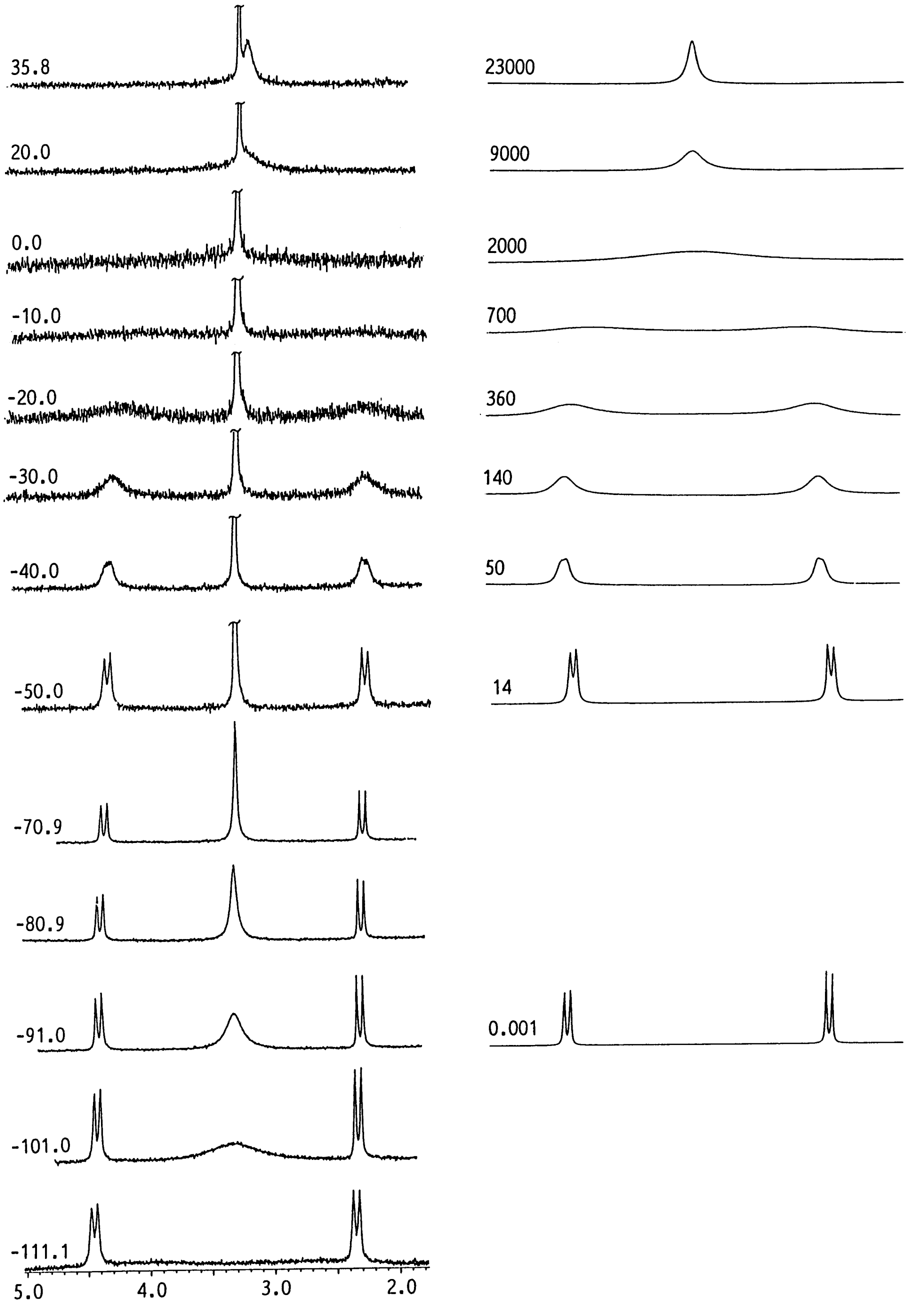


Fig. 2. 270 MHz spectra of the methylene protons of **1** at various temperatures (°C) in CD_2Cl_2 (left) and the calculated spectra for the minor isomer **B** with rate constants (sec^{-1}) (right).

Of another interest is the behavior of the methylene proton signals (Fig. 2). The methylene protons of the minor isomer (**B**) appear as a very broad signal at room temperature, but as an AB-quartet (δ 2.35 and 4.45, J=13.2 Hz) at -111 °C. This behavior is reasonably ascribed to the flipping of the methylene bridge. Lineshape analysis of the spectra in the temperature range of 35.8 to -50.0 °C using the DNMR3 program[9] followed by the least-squares analysis of the Eyring plot afforded the following kinetic parameters: $\Delta H^{\ddagger}=11.2\pm0.4$ kcal mol^{-1}, $\Delta S^{\ddagger}=-2.2\pm1.6$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{200K}=11.6_{8}$ kcal mol^{-1}. The methylene signal of the major isomer (**A**) appears as a sharp singlet at δ 3.29 at room temperature, which broadens on lowering the temperature and disappears under the baseline at -111 °C, the lowest attainable temperature. The free energy of activation for this process is estimated to be 7.1 kcal mol^{-1} at -111 °C if the same chemical shift difference as that of the minor isomer is assumed.

The large difference in the energy barriers between the two isomers is interesting. Temperature dependence of the olefinic proton chemical shifts seems to give some indication on this point. On lowering the temperature, the inner protons shift further down-field and the outer protons up-field. The degree of the signal movement is larger in the minor isomer **B** than in the major isomer **A**.[10] This suggests that **B** has higher rigidity of the skeleton to accommodate higher paratropicity while **A** is far more flexible. Isomer **A** may therefore more easily relieve the strain at the transition state of the methylene flipping and hence has a lower barrier.[11]

This work was partly supported by a Grant-in-Aid (No. 61470023) for Scientific Research from the Ministry of Education, Science and Culture.

References

1) For example: F. Sondheimer, Proc. R. Soc. London, Ser. A, 297, 173 (1967); I. C. Calder and P. J. Garratt, J. Chem. Soc., B, 1967, 660.
2) a) K. Yamamoto, M. Shibutani, S. Kuroda, E. Ejiri, and J. Ojima, Tetrahedron Lett., 27, 975 (1986); b) J. Ojima, E. Ejiri, T. Kato, M. Nakamura, S. Kuroda, S. Hirooka, and M. Shibutani, J. Chem. Soc., Perkin Trans. 1, 1987, 831; c) S. Kuroda, Y. Nozawa, Y. Yoneyama, S. Fujita, K. Yanagihara, and J. Ojima, Chem. Lett., 1987, 1679; d) J. Ojima, M. Masumoto, S. Kuroda, S. Hirooka, and Y. Nozawa, Bull. Chem. Soc. Jpn., 60, 3803 (1987); e) J. Ojima, S. Fujita, M. Masumoto, E. Ejiri, T. Kato, S. Kuroda, Y. Nozawa, S. Hirooka, Y. Yoneyama, and H. Tatemitsu, J. Chem. Soc., Perkin Trans. 1, 1988, 385; f) K. Yamamoto, S. Kuroda, M. Shibutani, Y. Yoneyama, J. Ojima, S. Fujita, E. Ejiri, and K. Yanagihara, ibid., 1988, 395.
3) P. J. Garratt, "Aromaticity," Wiley, New York (1986), p. 195.
4) K. Dimroth, H. Follmann, and G. Pohl, Chem. Ber., 99, 642 (1966).
5) It may be inferred that the formation ratio upon synthesis is close to the equilibrium ratio and the work-up processes including recrystallization perturb the isomer ratio.
6) Attempts to separate the isomers have not been successful so far. Preparative gel permeation chromatography gave a single broad peak even after 50 recycles. The early and later parts of the peak showed slightly different isomer ratio.
7) While the chemical shifts can be unambiguously assigned for **B** as shown in Scheme 1, two sets of assignments are possible for **A** and those shown in the Scheme is tentatively chosen, assuming that H-2 and H-26 resonate at lower field than H-9 and H-16 by analogy of **B** and methanothia[19]annulene.[2c]
8) Examination of Dreiding models of the isomers reveals that **B** is far less strained than **B'**.
9) D. A. Kleier and G. Binsch, QCPE, No. 165.
10) For example, H-6 of **B** which appears at δ 7.81 at 20 °C in CD_2Cl_2 moves to δ 8.41 at -111 °C, while H-6 of **A** appears at δ 7.53 at 20 °C and at δ 7.64 at -111 °C.
11) The energy barrier to ring inversion of cycloheptatriene itself is reported to be 6.1 kcal mol^{-1}: F. A. L. Anet, J. Am. Chem. Soc., 86, 458 (1964); F. R. Jensen and L. A. Smith, ibid., 86, 956 (1964).

(Received February 21, 1989)